

Wavelengths of the $3d^6(^5D)4s\,a^6D - 3d^6(^5D)4p\,y^6P$ Multiplet of Fe II (UV 8)

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We investigate the wavenumber scale of Fe I and Fe II lines using new spectra recorded with Fourier transform spectroscopy and using a re-analysis of archival spectra. We find that standards in Ar II, Mg I, Mg II and Ge I give a consistent wavenumber calibration. We use the recalibrated spectra to derive accurate wavelengths for the a^6D-y^6P multiplet of Fe II (UV 8) using both directly measured lines and Ritz wavelengths. Lines from this multiplet are important for astronomical tests of the invariance of the fine structure constant on a cosmological time scale. We recommend a wavelength of 1608.45081 Å with a one standard deviation uncertainty of 0.00007 Å for the $a^6D_{9/2} - y^6P_{7/2}$ transition.

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1. Introduction

The universality and constancy of the laws of nature rely on the invariance of the fundamental constants. However, some recent measurements of quasar (Quasi-stellar objects - QSO) absorption line spectra suggest that the fine-structure constant, α , [1] may have had a different value during the early universe [2]. Other measurements (e.g. [3]) do not show any change. The attempt to resolve these discrepancies can probe deviations from the standard model of particle physics and thus provide tests of modern theories of fundamental interactions that are hard to attain in other ways.

QSO absorption lines are used in these investigations to measure the wavelength separations of atomic lines in spectra of different elements - the many-multiplet method [4] - and compare their values at large redshifts with their values today. Any difference in the separations would suggest a change in α . Since this method uses many different species in the

analysis that have differing sensitivities to changes in α , it can be much more sensitive than previous methods, such as the alkali-doublet method [5], that use just one species. However, it requires very accurate laboratory wavelengths to be used successfully, since the observed changes in α are only a few parts in 10^5 , requiring laboratory wavelengths to 1:10⁷ or better. This has led to several recent measurements of ultraviolet wavelengths using both Fourier transform (FT) spectroscopy [6–8] and frequency comb metrology [9–11].

One spectral line of particular interest is the $3d^6(^5D)4s\,a^6D_{9/2} - 3d^5(^6S)4s4p(^3P)\,y^6P_{7/2}$ line of Fe II at 1608.45 Å. This line is prominent in many QSO spectra and its variation with α has the opposite sign from that of other nearby lines [12]. However, measurement of its wavelength using frequency comb metrology, which is at present the most accurate method, is extremely difficult due to its short wavelength. Although this line is strong in many of the FT spectra of iron-neon hollow cathode lamps recorded at the National Institute of Standards and Technology (NIST) and Imperial College, London, UK (IC), these spectra display inconsistencies in the wavelength of the 1608 Å line of around 1.5 parts in 10^7 - too great for use in the many-multiplet method to detect changes in α . We discussed some of these discrepancies in our previous paper [13] presenting reference wavelengths in the spectra of iron, germanium and platinum around 1935 Å.

Here we present a re-analysis of spectra taken at NIST and IC in order to resolve these discrepancies and provide a better value for the wavelength of the 1608.45 Å line of Fe II. The papers involved in this re-analysis are listed in table 1, together with the proposed corrections to the wavenumber scale. The proposed corrections are up to three times the previous total uncertainty, depending on the wavenumber. In section 2 we discuss previous measurements of the $a^6D - y^6P$ multiplet. Section 3 describes the archival data we use to obtain improved wavelengths for this multiplet. Additional spectra taken at NIST in order to re-evaluate the calibration of these archival data are described in section 4. The accuracy of this calibration in the visible and ultraviolet wavelength regions is also discussed in section 4. Section 5 describes three different methods for obtaining the wavelengths of the $a^6D - y^6P$ multiplet. The first method uses intermediate levels determined using strong Fe II lines in the visible and ultraviolet in order to obtain the values of the y^6P levels and Ritz wavenumbers for the $a^6D - y^6P$ multiplet. The second method uses energy levels optimized by using a large number of spectral lines to derive Ritz wavenumbers for this multiplet. Although better accuracy is achieved using this method than the first method because of the increased redundancy, the way in which the y^6P levels are determined is less transparent. The third method uses experimental wavelengths determined in spectra that are recalibrated from spectra in which we have re-evaluated the wavenumber calibration. In section 6 we re-examine the Fe II wavenumbers in our previous paper [13]. All uncertainties in this paper are reported at the one standard deviation level.

2. Previous measurements of the $a^6D - y^6P$ multiplet

The region of the $a^6D - y^6P$ multiplet is shown in figure 1 as observed in a FT spectrum taken at IC. Nave, Johansson & Thorne [14] report Ritz and experimental wavelengths for six of the nine lines of the $a^6D - y^6P$ multiplet. The Ritz wavelengths are based on energy levels optimized to spectral lines covering wavelengths from 1500 Å to 5.5 μm measured with FT spectroscopy. The estimated uncertainties are about 2×10^{-4} Å or about 1.2 parts in 10^7 . The published lines do not include the $a^6D_{9/2} - y^6P_{7/2}$ line. Johansson [15] contains Ritz wavelengths for all nine lines, based on unpublished interferometric measurements of Norlén, with a value of 1608.451 Å for this line. The estimated uncertainty of the $y^6P_{7/2}$ level with respect to the ground state $a^6D_{9/2}$ of Fe II is 0.02 cm^{-1} . The uncertainty of the 1608 Å line can be derived directly from the uncertainty of the $y^6P_{7/2}$ level, and corresponds to a wavelength uncertainty at 1608 Å of 0.0005 Å. Wavelengths for all nine lines measured using FT spectroscopy are also given in Pickering et al. [16] in a paper devoted to oscillator strength measurements. No details of the calibration of these lines or their uncertainties are given. The wavelength value recommended by Murphy et al. [12] is 1608.45080 ± 0.00008 Å, with a reference to Pickering et al. However, this is not the value given in Pickering et al. and the small uncertainty is improbable without additional confirmation. The source of this wavelength is unclear.

In addition to these published values, lines from this multiplet are present in some unpublished archival spectra from IC and NIST. The most important spectra for the current work are summarized in Table 2. The spectra on which Nave, Johansson & Thorne [14] is based are part of a much larger set of Fe II spectra covering all wavelengths from 900 Å to 5.5 μm. Two of these spectra cover the region around 1600 Å and contain all nine lines of the multiplet. The wavelength standards for these spectra are traceable to a set of Ar II lines between 3729 Å and 5146 Å (see section 4 for details). The weighted average wavelength for the $a^6D_{9/2} - y^6P_{7/2}$ line in these unpublished archival spectra is 1608.45075 ± 0.00018 Å.

The spectra in Nave & Sansonetti [13] were calibrated with respect to Ge standards of Kaufman & Andrew [17]. In addition to the spectra used in that paper, we recorded a spectrum using FT spectroscopy with a pure iron cathode that covers the wavelength region of the $a^6D - y^6P$ multiplet (fe1115 in Table 2). It was calibrated with iron lines measured in one of the spectra used for ref. [13] (lp0301 in Table 2). The resulting value for the wavelength of the $a^6D_{9/2} - y^6P_{7/2}$ line was 1608.45050 ± 0.00004 Å, 1.5×10^{-7} times smaller than the wavelength obtained from the archival spectra and outside their joint uncertainty. This inconsistency is also larger than the uncertainty required for measurements of possible changes in α .

3. Summary of current experimental data

The spectra we re-analyzed are the same as those used in previous studies of Fe I and Fe II [13, 14, 18, 19]. Three different spectrometers were used: the f/60 IR-visible-UV FT spectrometer at the National Solar Observatory, Kitt Peak, AZ (NSO), the f/25 vacuum ultraviolet (VUV) FT spectrometer at IC [20], and the f/25 VUV spectrometer at NIST [21]. The light sources for all of the spectra were high-current hollow cathode lamps containing a cathode of pure iron run in either neon or argon. Gas pressures of 100 Pa to 500 Pa (0.8 Torr to 4 Torr) were used with currents from 0.32 A to 1 A. The total number of FT spectra was 31, covering wavelengths from about 1500 Å to 5 μm (2000 cm⁻¹ to 66000 cm⁻¹). The wavenumber, intensity and width for all the lines were obtained with Brault’s DECOMP program [22] or its modification XGREMLIN [23]. Further details of the experiments can be found in [13, 14, 18, 19]. Additional spectra were taken using the NIST 2-m FT spectrometer and are described in section 4.A.

4. Calibration of FT spectra

All of the spectra were calibrated assuming a linear FT wavenumber scale, so that in principle only one reference line is required to put the measurements on an absolute scale. In practice, many lines are used. To obtain the absolute wavenumbers, a multiplicative correction factor, k_{eff} , is derived from the reference lines and applied to each observed wavenumber σ_{obs} so that

$$\sigma_{\text{corr}} = (1 + k_{\text{eff}})\sigma_{\text{obs}} \quad (1)$$

where σ_{corr} is the corrected wavenumber.

All the spectra in Learner & Thorne (3830 Å to 5760 Å) [18] and Nave et al. (1830 Å to 3850 Å) [19] trace their calibration to 28 Ar II lines in the visible. The original calibration in Refs. [18] and [19] used the wavenumbers of Norlén [24] for these lines. Norlén calibrated these Ar II lines with respect to ⁸⁶Kr I lines emitted from an electrodeless microwave discharge lamp that had in turn been calibrated with respect to an Engelhard lamp, which was the prescribed source for the primary wavelength standard at the time of his measurements. The estimated standard uncertainty of Norlén’s Ar II wavenumbers varies from 0.0007 cm⁻¹ at 19429 cm⁻¹ to 0.001 cm⁻¹ at 22992 cm⁻¹. The Ar II lines were used to calibrate a ‘master spectrum’ (spectrum k19 in Table 2). Additional spectra of both Fe-Ne and Fe-Ar hollow cathode lamps covering wavelengths from 2778 Å to 7387 Å were calibrated from this master spectrum.

The ultraviolet spectra reported in [19] were calibrated with respect to the results of Learner & Thorne [18] by using a bridging spectrum. This bridging spectrum used two different detectors, one on each output of the FT spectrometer. The first overlapped with the visible wavenumbers in Ref. [18] in order to obtain a wavenumber calibration and the

second covered the UV wavenumbers being measured. Since the two outputs of the FT spectrometer are not exactly in antiphase, the resulting phase correction has a discontinuity in the region around $35\,000\text{ cm}^{-1}$ where the two detectors overlap, as shown in Fig. 1 of [19]. The full procedure is described in detail in [19].

The 28 Ar II lines used as wavenumber standards in Refs. [18, 19] were subsequently re-measured by Whaling et al. [25] using FT spectroscopy with molecular CO lines as standards. The uncertainty of these measurements is 0.0002 cm^{-1} . The molecular CO standards used in Ref. [25] were measured using heterodyne frequency spectroscopy with an uncertainty of around $1:10^9$ and are ultimately traceable to the cesium primary standard [26]. The wavenumbers of Whaling et al. [25] are systematically higher than those of Norlén [24] by 6.7 ± 0.8 parts in 10^8 , corresponding to a wavenumber discrepancy of about 0.0014 cm^{-1} at 21000 cm^{-1} . Since the results of Whaling et al. [25] are more accurate and precise than those of Norlén [24], all the wavenumbers in [18], [19], and Table 3 of [14] have been increased by 6.7 parts in 10^8 wherever they are used in the current work.

The spectra in Nave & Sansonetti [13] were calibrated with respect to 29 Ge I Ritz wavenumbers derived from the energy levels of Kaufman & Andrew [17]. However, the Fe II wavenumbers derived using this calibration were found to be greater than those in Nave et al. [19] by about 7 parts in 10^8 , even after the wavenumbers in the latter were adjusted to the wavenumber scale of Whaling et al. [25].

In order to present accurate wavenumbers for Fe II lines around 1600 Å , it is necessary first to confirm the accuracy of the iron lines in the visible that were calibrated with respect to selected lines of Ar II lines [18], to investigate the accuracy with which this calibration is transferred to the VUV, and to resolve the discrepancy between iron and germanium standard wavelengths identified in Ref. [13].

4.A. Calibration of the visible-region spectra

In order to confirm the calibration of the master spectrum, k19, used in [18] and [19], we took additional spectra using the NIST 2 m FT spectrometer [23]. The source was a water-cooled high-current hollow cathode lamp with a current of 1.5 A and argon at pressures of 130 Pa to 330 Pa (1 Torr to 2.5 Torr). The spectra covered the region 8500 cm^{-1} to $37\,000\text{ cm}^{-1}$ with resolutions of either 0.02 cm^{-1} or 0.03 cm^{-1} . A 1 mm aperture was used in order to minimize possible illumination effects. The detector was a silicon photodiode detector with a $2\text{ mm} \times 2\text{ mm}$ active area.

The spectrometer was aligned optimally using a diffused, expanded beam from a helium neon laser, ensuring that the modulation of the laser fringes was maximized throughout the 2 m scan. Before recording some of the spectra, the spectrometer was deliberately misaligned and re-aligned in order to test whether small misalignments that could not be detected using

our alignment procedure affected the wavenumber scale.

The spectra were calibrated using the values of Whaling et al. [25] for Ar II lines recommended in Ref. [18] that had good signal-to-noise ratio. Wavenumbers of strong iron lines were then measured and compared with iron lines taken from Ref. [18] and [19].

Figure 2 shows the calibration of one of our spectra using Ar II and iron lines from Refs. [18,19,25] as standards. The calibration constant k_{eff} does not depend on wavenumber and is the same for all three sets of standards to within $1:10^8$ when the iron lines from the Refs [18,19] are adjusted to the wavenumber scale of [25]. The possibility of shifts due to non-uniform illumination of the aperture were investigated by taking a spectrum with the 5 mm diameter image of the hollow cathode lamp offset from the 1 mm aperture by about 2 mm. This spectrum also shows good agreement between the Ar II and iron calibrations.

Many of the early interferograms from the NSO FT spectrometer were asymmetrically sampled, with a much larger number of points on one side of zero optical path difference than the other. A Fourier transform of an asymmetrically-sampled interferogram gives a spectrum with a large, antisymmetric imaginary part [27]. A small error in the phase correction causes a small part of this antisymmetric imaginary part to be rotated into the real part of the spectrum, distorting the line profiles and causing a wavenumber shift. The zero optical path difference in spectrum k19 is roughly 1/5 of the way through the interferogram. For a Gaussian profile with a full width at half maximum of W , this produces a wavenumber shift of roughly $0.3W$ per radian of phase error as shown in Fig. 3 of [27].

We decided to re-examine the phase curve for the master spectrum, k19, against which all the other iron spectra used in [14,18,19] were calibrated. The original interferogram for this spectrum was obtained from the NSO Digital Archives [28] and re-transformed using Xgremlin. The phase is plotted in Fig. 3. The residual phase error after fitting an 11th order polynomial is less than 10 mrad for almost all wavenumbers below $35\,000\text{ cm}^{-1}$. This corresponds to an error of $3.6 \times 10^{-4}\text{ cm}^{-1}$ for a linewidth of 0.12 cm^{-1} . Above $35\,000\text{ cm}^{-1}$ the polynomial no longer fits the points adequately and consequently these points were not used in the comparison. Wavenumbers were measured in the re-transformed spectrum and calibrated with the 28 Ar II lines recommended in Ref. [18] using the values of Ref. [25]. Iron lines were then compared with those from papers [18,19]. The result is shown in Fig. 4. The two measurements agree to within $1:10^8$. This confirms that the original phase correction of k19 was accurate and the wavenumbers in Ref. [18] and Table 3 of Ref. [19] (2929 \AA to 3841 \AA) are not affected by phase errors.

We conclude that the wavenumbers measured in the master spectrum, k19, are accurate. Although results from this spectrum were used in Learner & Thorne [18] and Table 3 of Nave et al. [19], it did not dominate the weighted average values reported in these papers.

4.B. Calibration of the ultraviolet spectra

Tables 4 and 5 in Nave et al. [19] cover wavenumbers from $33\,695\text{ cm}^{-1}$ to $54\,637\text{ cm}^{-1}$ in Fe I and Fe II respectively. The wavenumbers in these tables were measured using the vacuum ultraviolet FT spectrometer at IC. The calibration of these spectra was transferred from the master spectrum (k19 in Table 2) using a bridging spectrum (i56 in Table 2), as described in section 4. The principal spectrum covering wavenumbers below $35\,000\text{ cm}^{-1}$ in Table 4 of [19] is i6 in Table 2. It overlaps with the master spectrum between $33\,000\text{ cm}^{-1}$ and $34\,000\text{ cm}^{-1}$. Figure 5 shows a comparison of wavenumbers in i6 with the master spectrum k19. The wavenumbers in spectrum i6 are systematically smaller than in k19 by 3.9 ± 0.5 parts in 10^8 . Although the region of overlap of i6 with k19 is small and is thus insensitive to non-linearities in the wavenumber scale, this result supports our earlier speculation in Nave & Sansonetti [13] that the calibration of the UV data using the bridging spectrum may be incorrect. Based on the comparison of Fig 5, we conclude the wavenumbers in Tables 4 and 5 of Ref. [19] should be increased by 10.6 parts in 10^8 , consisting of 3.9 parts in 10^8 to correct the transfer of the calibration to the ultraviolet and an additional 6.7 parts in 10^8 to put all the spectra on the wavenumber scale of Whaling et al. [25].

We compared our corrected values for iron lines in the UV to results of Aldenius et al. [7,8], who present wavenumbers of iron lines measured in a high-current hollow cathode lamp using a UV FT spectrometer similar to the one used in [19]. Instead of recording a pure iron spectrum, they included small pieces of Mg, Ti, Cr, Mn and Zn in their Fe cathode. This ensured that spectral lines due to all of these species were placed on the same wavenumber scale, which was calibrated using the Ar II lines of Whaling et al. [25]. Table 3 compares the wavenumbers of Ref. [8] with the corrected values of [19]. Although the wavenumbers of Ref. [8] agree with our revised values within their joint uncertainties, they are systematically smaller by 3.7 parts in 10^8 . Although this might suggest that it is incorrect to increase the wavenumbers of Ref. [19], it might also indicate that the wavenumbers of Ref. [8] need to be increased.

Fortunately, there are data that allow us to test these alternatives. In addition to iron lines, the spectra in Ref. [8] contained four lines due to Mg I and Mg II that have since been measured using frequency comb spectroscopy [9–11] with much higher accuracy than achievable using FT spectroscopy. Table 4 compares the wavenumbers of these four magnesium lines from [8] with those derived from frequency comb measurements of isotopically pure values. For this comparison, the results of [8] have been increased by 3.7 parts in 10^8 , as suggested by the comparison of Fe II lines in Table 3. With this adjustment, the results of Aldenius agree with the frequency comb values within their joint uncertainties, having a mean deviation of -0.7 ± 3 parts in 10^8 . Without the adjustment the mean deviation would be $(-4\pm3)\times10^{-8}$.

We conclude that the wavenumbers in Tables 4 and 5 of Nave et al. [19] should be increased by 10.6 parts in 10^8 : 3.9 parts in 10^8 to correct for the incorrect transfer of the calibration from the master spectrum to the ultraviolet and 6.7 parts in 10^8 to put all of the spectra on the scale of Whaling et al. [25]. We have performed this correction in the following sections of the current paper. The wavenumbers of Aldenius et al. [8] should be increased by 3.7 parts in 10^8 to put them on the same scale. This adjustment of scale brings the measurements of lines of Mg I and Mg II in [8] into agreement with the more accurate frequency comb values [9–11].

5. Wavenumbers of $a^6D - y^6P$ transitions

The wavenumbers of the $a^6D - y^6P$ transitions can be obtained either from direct measurements or from energy levels derived from a larger set of experimental data (Ritz wavenumbers). Direct measurements will have larger uncertainties due to the cumulative addition of the uncertainties in the transfer of the calibration from the visible to the UV. Ritz wavenumbers are more accurate due to the increased redundancy, but use of a large set of experimental data to derive the energy levels makes it less clear exactly how the Ritz wavenumbers are derived. We illustrate this process by using a small subset of the strongest transitions that determine the y^6P levels that are present in the visible and ultraviolet regions of the spectrum where we have corrected the wavenumber calibration.

The y^6P levels can be determined from three sets of lines in the UV and visible as shown in Fig. 6. The first set of nine lines near 2350 Å determines the three $3d^6(^6D)4p\,z^6P$ levels. All nine lines are present in archival spectra from IC which we have recalibrated using the results of section 4.B. Two of the nine lines are blended with other lines and a third, between $a^6D_{9/2}$ and $z^6P_{7/2}$, is self-absorbed in the IC spectra. These lines are unsuitable for determining the z^6P levels. The recalibrated values of the remaining six lines are shown in column 4 of Table 5. Each line is observed with a signal-to-noise ratio of over 100 in at least eight spectra, all of which agree within 0.006 cm^{-1} . The wavenumbers in Table 5 are weighted mean values of the individual measurements and the standard deviation in the last decimal place is given in parenthesis following the wavenumber. The lower levels in column 3 are determined from between 10 and 20 different transitions to upper levels and have been optimized to the archival spectra with the program LOPT [29] (described below). The total standard uncertainty in the upper levels includes the calibration uncertainty of 2.3×10^{-8} times the level value.

The second set of three transitions around 5000 Å determines the $3d^54s^2\,a^6S_{5/2}$ level from the three z^6P levels. These lines are present in k19 and other archival spectra taken at NSO that we have recalibrated to correspond to the wavenumber scale of Whaling et al. [25]. Each line is present in five spectra, all of which agree within 0.0035 cm^{-1} . Wavenumbers for these

transitions are shown in Table 6 and give a mean value of (23317.6344 ± 0.0010) cm^{-1} for the $3d^5 4s^2 \text{a}^6\text{S}_{5/2}$ level.

Finally, the y^6P levels can be determined from the $\text{a}^6\text{S}_{5/2}$ level from three lines around 2580 Å, present in the IC spectra. The recalibrated wavenumbers are shown in Table 7 with the resulting y^6P level values. These values were used to calculate Ritz wavenumbers for the $\text{a}^6\text{D} - \text{y}^6\text{P}$ transitions, as shown in the third column of Table 8.

Alternate values for the Ritz wavenumbers of the $\text{a}^6\text{D} - \text{y}^6\text{P}$ transitions can be obtained from energy levels optimized using wavenumbers from the archival Fe II spectra from NSO and IC corrected according to sections 4.A and 4.B. The program LOPT [29] was used to derive optimized values for 939 energy levels from 9567 transitions. Weights were assigned proportional to the inverse of the estimated variance of the wavenumber. Lines with more than one possible classification, lines that were blended, or for which the identification was questionable were assigned a low weight. Two iterations were made. In the first, lines connecting the lowest a^6D term to higher $3d^6 ({}^5\text{D})4p$ levels were assigned a weight proportional to the inverse of the statistical variance of the wavenumber, omitting the calibration uncertainty. This was done to obtain accurate values and uncertainties for the a^6D intervals. These intervals are determined from differences between lines close to one another in the same spectrum sharing the same calibration factor. Hence the calibration uncertainty does not contribute to the uncertainty in the relative values of these energy levels. The values of the a^6D levels obtained in this iteration are given in column 3 of table 5. In the second iteration, the a^6D levels were fixed to the values and uncertainties determined from the first iteration. The weights of the $\text{a}^6\text{D} - 3d^6 ({}^5\text{D})4p$ transitions were assigned by combining in quadrature the statistical uncertainty in the measurement of the line position and the calibration uncertainty in order to obtain accurate uncertainties for the $3d^6 ({}^5\text{D})4p$ and higher levels. The values of the y^6P levels are given in column 4 of table 7. Ritz wavenumbers for the $\text{a}^6\text{D} - 3d^6 ({}^5\text{D})4p$ transitions based on these globally optimized level values are presented in column 5 of table 8.

The corrected experimental wavenumbers from the archival spectra are given in column 4 of table 8. The main contribution to the uncertainty in the experimental wavenumbers is from the calibration and consists of two components – the uncertainty in the standards and the uncertainty in calibrating the spectrum. The calibration uncertainty is common to all lines in the calibrated spectrum and hence must be added to the uncertainties of wavenumbers measured using transfer standards, rather than added in quadrature as would be the case for random errors. Hence the uncertainty in the wavenumbers increases with each calibration step, resulting in larger uncertainties at the shortest wavenumbers which are furthest from the calibration standards. The experimental standard uncertainties in Table 8 are determined by combining in quadrature the statistical uncertainty in determining the

line position and the calibration uncertainty of 4×10^{-8} times the wavenumber. The experimental wavenumber and both Ritz wavenumbers agree within their joint uncertainties. The Ritz wavenumbers determined from optimized energy levels have the smallest uncertainties. Wavelengths corresponding to these wavenumbers are given in column 7.

6. A re-examination of Fe II wavenumbers from Nave & Sansonetti [13]

The Fe I lines in Nave & Sansonetti [13] were calibrated with respect to lines of Ge I. Figure 3 of that paper showed that the calibration factor k_{eff} derived from Fe I and Fe II lines is smaller than that derived from Ge I by 6.5 parts in 10^8 . We attributed this to a possible problem in the transfer of the wavenumber calibration of the Fe I and Fe II lines from the region of the Ar II wavenumber standards to the vacuum ultraviolet, thus suggesting that the wavenumber standards in [19] are too small. In section 4.B we have confirmed that the wavenumbers in Tables 4 and 5 of Nave et al. [19] should be increased by 3.9 parts in 10^8 due to the transfer of the calibration. This reduces but does not fully explain the calibration discrepancy in [13].

The Ge I lines used to calibrate the spectra in Ref. [13] were measured by Kaufman and Andrew [17]. The wavenumber standard they used was the 5462 Å line of ^{198}Hg emitted by an electrodeless discharge lamp maintained at a temperature of 19 °C, containing Ar at a pressure of 400 Pa (3 Torr). The vacuum wavelength of this line was assumed to be 5462.27075 Å. This value was based on a vacuum wavelength of 5462.27063 Å measured in the same lamp at 7 °C [30], with an adjustment for the different temperature using the measurements of Emara [31]. The 5462 Å line was remeasured by Salit et al. [32] using a temperature of 8 °C. A value of (5462.27085 ± 0.00007) Å was obtained. More recent work by Sansonetti & Veza [33] gives the wavelength of this line as 5462.270825(11) Å, in agreement with [32] but more precise. Adoption of this value for the wavelength of the ^{198}Hg line implies that all of the Ge I wavenumbers in [17] should be decreased by 1.4 parts in 10^8 . Figure 7 shows how Fig. 3 in [13] (Spectrum lp0301 in Table 2) changes with the adjustment of both the iron and germanium wavenumbers. The calibrations based on Ge and Fe lines now differ by only 1.5 parts in 10^8 , which is within the joint uncertainties. We thus conclude that the calibration derived from Fe I and Fe II lines is in agreement with that derived from Ge I when both sets of standards are adjusted to correspond with the most recent measurements.

Spectrum lp0301 in Table 2 can be used to calibrate spectrum fe1115 in Table 2 referred to in the last paragraph of section 2. A value of (62171.634 ± 0.006) cm^{-1} is obtained for the wavenumber of the $a^6\text{D}_{9/2} - y^6\text{P}_{7/2}$ line, corresponding to a wavelength of (1608.45057 ± 0.00016) Å. This disagrees with the Ritz value by 1.7 times the joint uncertainty and marginally disagrees with the experimental values of Table 8. The mean difference in the experimental values for all nine $a^6\text{D} - y^6\text{P}$ lines is (0.008 ± 0.004) cm^{-1} . We believe this

difference is due to a small slope in the calibration of lp0301 but have been unable to confirm this with our data. The principal contributors to the uncertainty are the uncertainty in the iron and germanium standards, the uncertainty in calibrating the spectrum in ref. [13] from these standards, and the uncertainty in calibrating spectrum fe1115 from spectrum lp0301.

7. Conclusions

We investigated the wavenumber scale of published Fe I and Fe II lines using new spectra recorded with the NIST 2-m FT spectrometer and a re-analysis of archival spectra. Our new spectra confirm the wavenumber scale of visible-region iron lines calibrated using the Ar II wavenumber standards of Whaling et al. [25].

Having confirmed the wavenumber scale of iron lines in the visible and ultraviolet regions, we have used lines from these spectra to derive Ritz values for the wavenumbers and wavelengths of lines in the $a^6D - y^6P$ multiplet of Fe II (UV 8). Ritz wavenumbers derived using two different methods agree with one another and with directly measured wavenumbers within the joint uncertainties. We recommend a value of 1608.45081 ± 0.00007 Å for the wavelength of the $a^6D_{9/2} - y^6P_{7/2}$ line of Fe II, which is an important line for detection of changes in the fine-structure constant during the history of the Universe using quasar absorption-line spectra.

We find that the wavenumbers in Learner & Thorne [18] and Table 3 of Nave et al. [19] should be increased by 6.7 parts in 10^8 to put them on the scale of the Ar II lines of Whaling et al. [25]. The wavenumbers in Tables 4 and 5 of Ref. [19] should be increased by 10.6 parts in 10^8 to put them on the Ar II scale of Ref. [25] and to correct for an error in the transfer of this wavenumber scale to the ultraviolet. The Ge I wavenumbers of Kaufman & Andrew [17] and all the wavenumbers in Nave & Sansonetti [13] should be decreased by 1.4 parts in 10^8 to put them on the scale of recent measurements of the ^{198}Hg line at 5462 Å.

8. Acknowledgments

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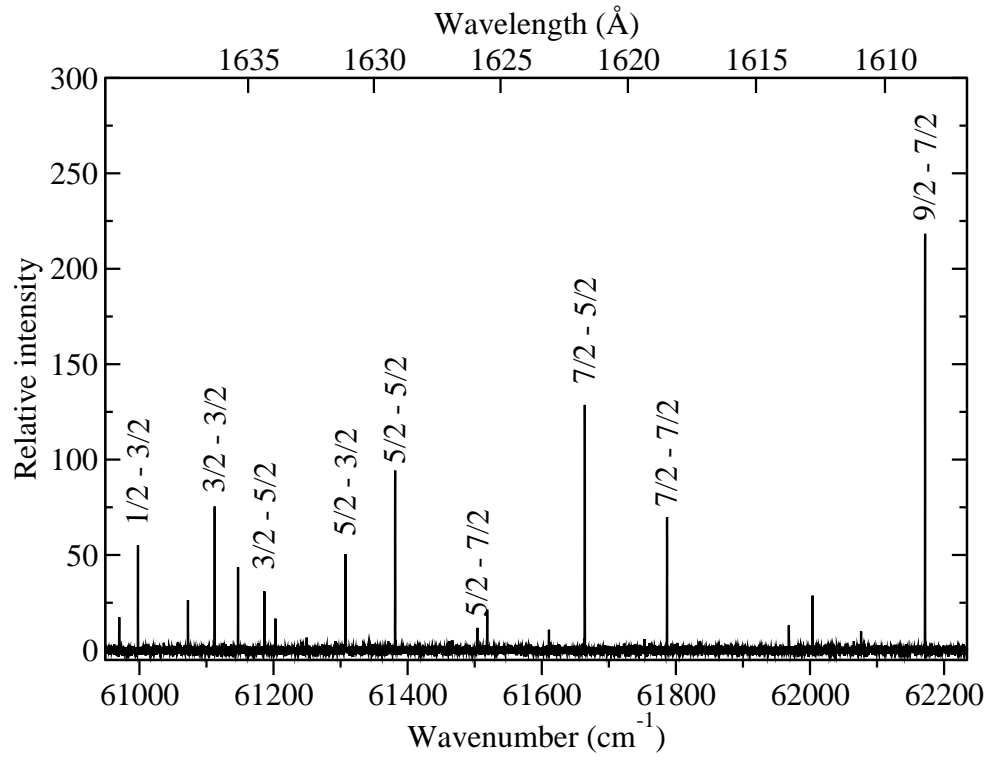


Fig. 1. The region of the Fe II $a^6D - y^6P$ transitions. The labeled lines show the J-values of the lower and upper energy levels respectively.

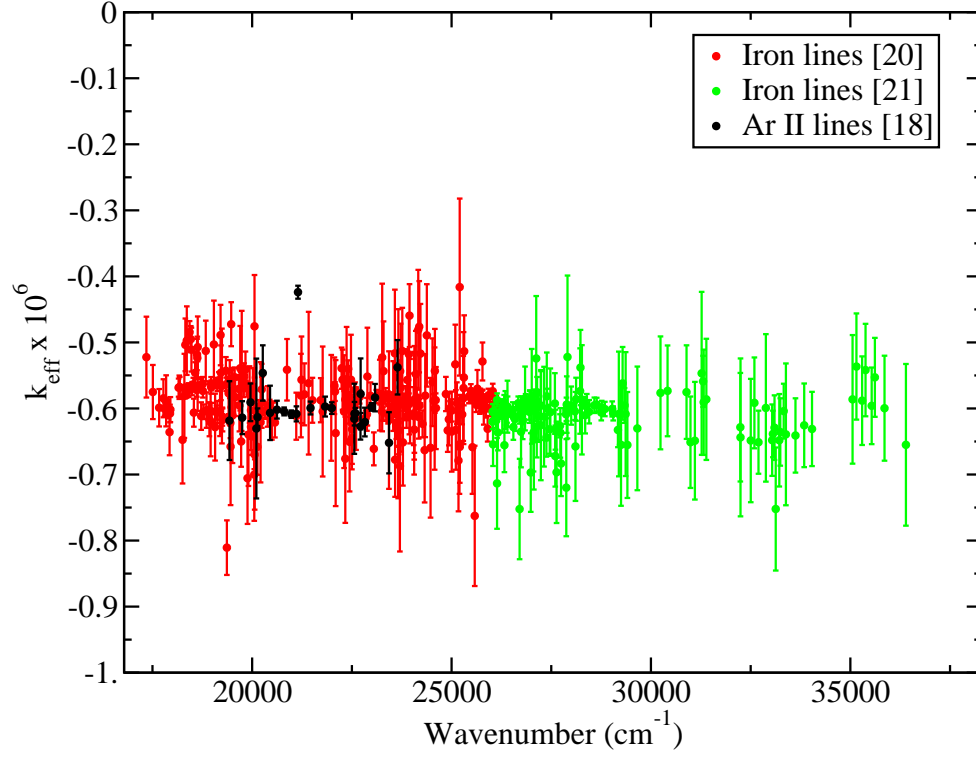


Fig. 2. (Color online) Calibration of wavenumbers in spectrum fe0409.002 in Table 2 using Ar II standards from [25], and iron standards taken from Learner & Thorne [18] and Nave et al. [19]. The error bars represent the statistical uncertainty in the measurement of the wavenumber.

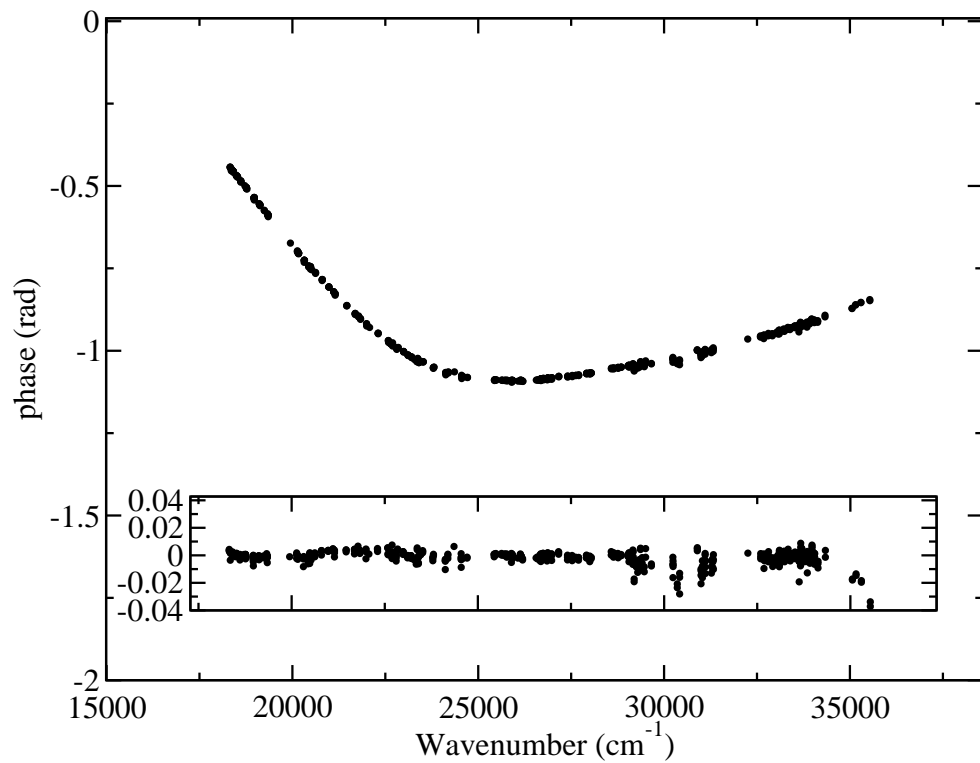


Fig. 3. Phase in the master spectrum, k19, used in Learner & Thorne [18]. The insert shows the residual phase after fitting the points to an 11th order polynomial.

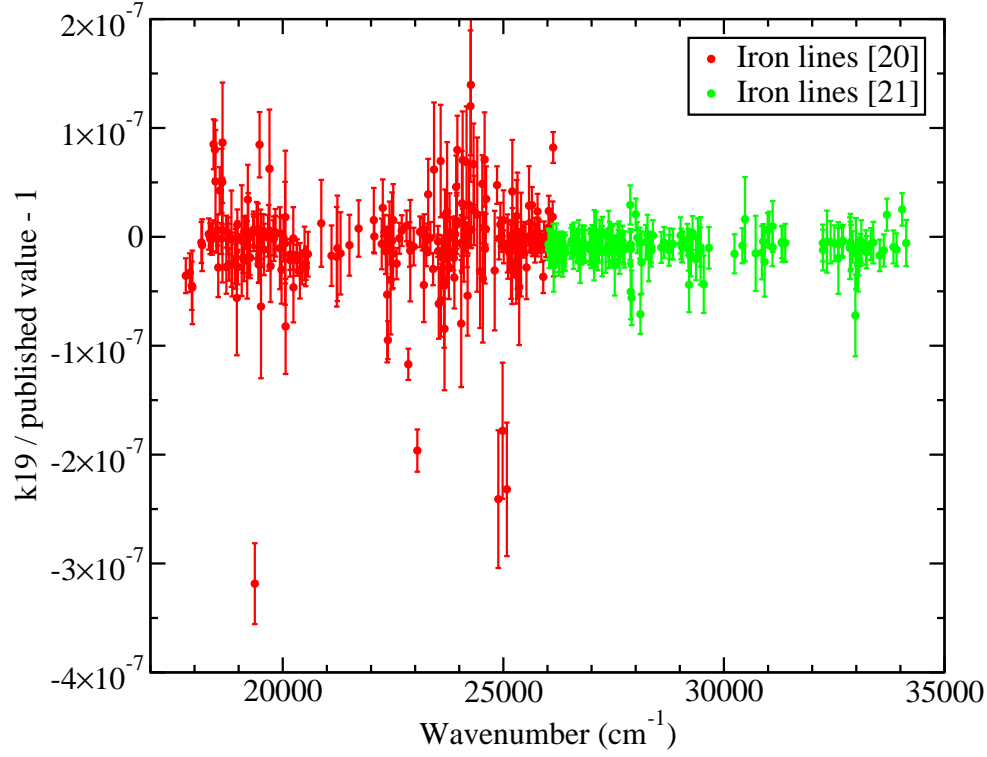


Fig. 4. (Color online) Comparison of wavenumbers in the master spectrum, k19, calibrated from Ar II standards from [25] with iron standards taken from [18] and [19] adjusted to the scale of [25]. The error bars represent the statistical uncertainty in the measurement of the wavenumber.

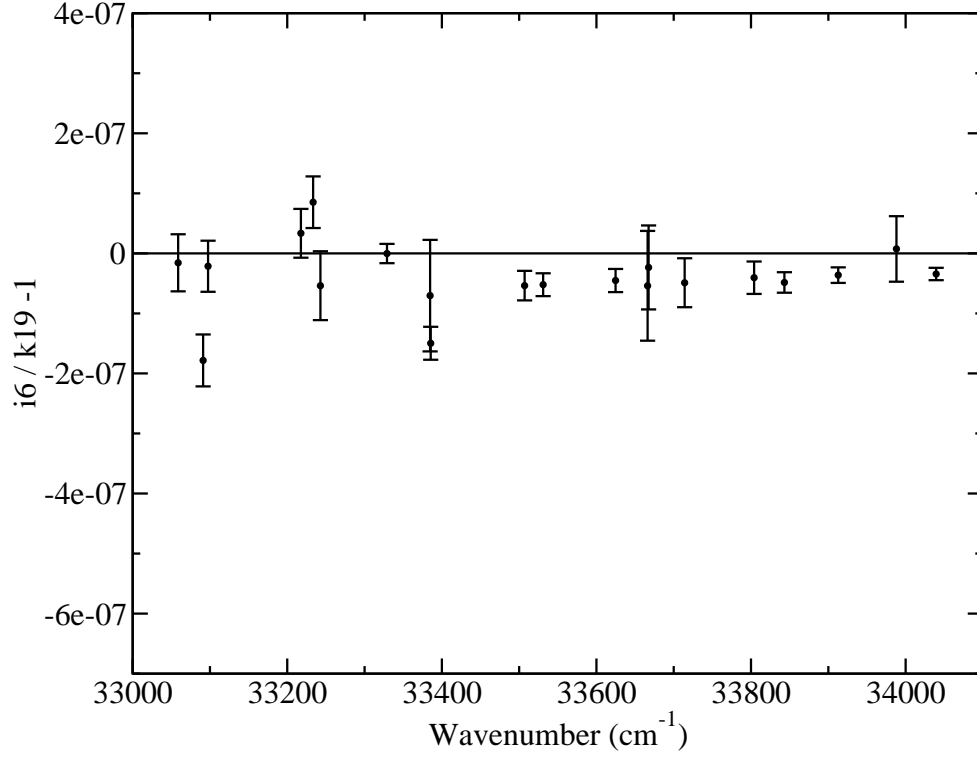


Fig. 5. Comparison of wavenumbers in the master spectrum, k19, with those in i6, the main spectrum contributing to Table 4 of [19] in this wavelength region.

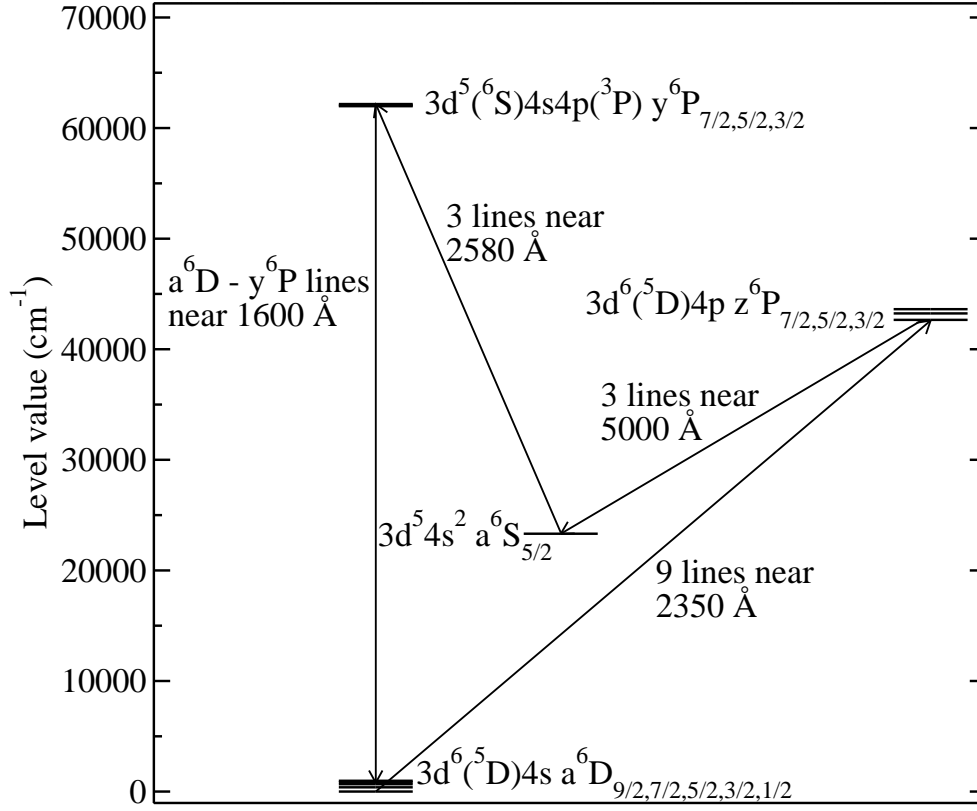


Fig. 6. Partial term diagram of Fe II showing the determination of the y^6P levels using transitions in the UV and visible regions

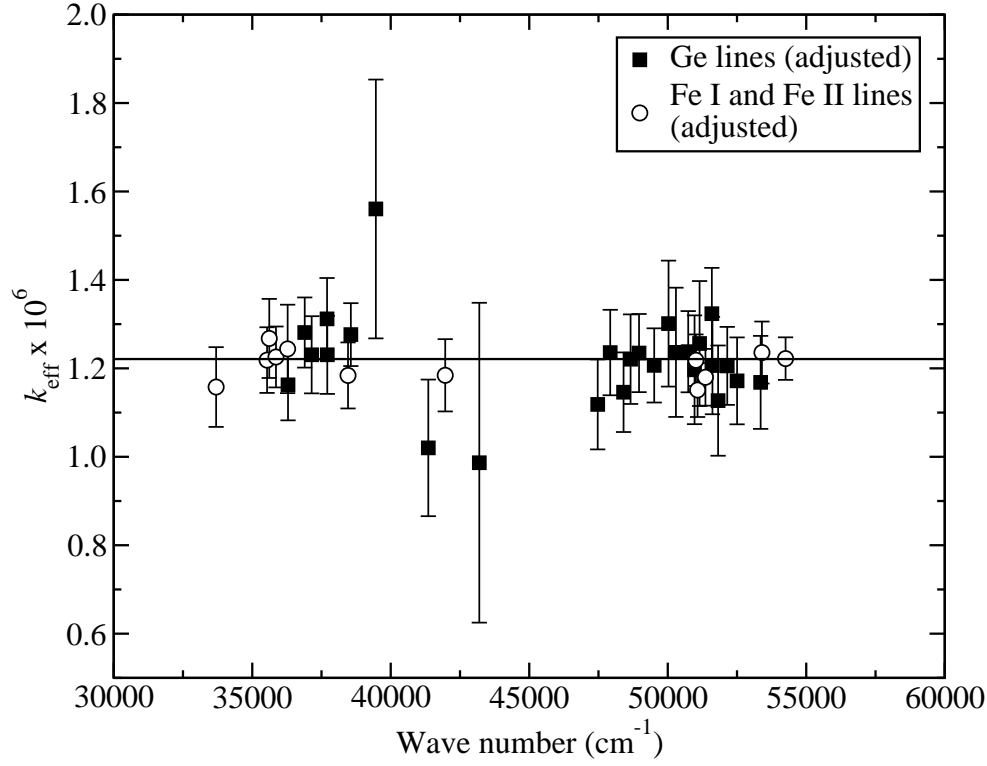


Fig. 7. Figure 3 from Nave & Sansonetti [13], with all of the Ge I wavenumbers reduced by 1.4 parts in 10^8 and the Fe I and Fe II wavenumbers increased by 3.9 parts in 10^8 . The mean value of k_{eff} for the Ge I wavenumbers is $(1.221 \pm 0.020) \times 10^{-6}$, in agreement within the joint uncertainties with the value of $(1.206 \pm 0.020) \times 10^{-6}$ from the Fe I and Fe II lines

Table 1. Proposed corrections to previous papers.

Reference	Wavenumber range (cm^{-1})	Previous standard	Previous uncertainty (cm^{-1})	New standard	Correction to wavenumber scale
[18]	17350 - 26140	Ar II [24]	0.001	Ar II [25]	$(+6.7 \pm 1.8) \times 10^{-8}$
Table 3 of [19]	26027 - 34131	Ar II [24], i56	0.002	Ar II [25]	$(+6.7 \pm 1.8) \times 10^{-8}$
Tables 4 & 5 of [19]	33695 - 54637	Ar II [24], i56	0.002	Ar II [25], Fig.5	$(+10.6 \pm 2.3) \times 10^{-8}$
[14]	50128 - 107887	Ar II [24], i56	0.005	Ar II [25], Fig.5	$(+10.6 \pm 2.3) \times 10^{-8}$
[13]	51613 - 51692	Ge I [17]	0.002	^{198}Hg [33]	$(-1.4 \pm 2) \times 10^{-8}$
[8]	38458 - 44233	Ar II [25]	0.002	Table 3,4	$(+3.7 \pm 3) \times 10^{-8}$
[17] (Ge I & Ge II)	8283 - 100090	^{198}Hg , [30, 31]	< 0.006	^{198}Hg [33]	$(-1.4 \pm 1.8) \times 10^{-8}$
[24] (Ar II) ^a	4348 - 5145	^{86}Kr Engelhard lamp	< 0.001	Ar II [25]	$(+6.7 \pm 0.8) \times 10^{-8}$

^aThe proposed correction has only been confirmed for the 28 Ar II lines recommended in [18].

Table 2. Summary of spectra

Spectrum	Instrument	Date y/m/d	Wavelength Range (\AA)	Calibration Spectrum	Comments
k19 [19]	NSO	81/07/22	2800 to 5600	Ar II [25]	810622R0.009 (NSO [28]) A1 in [18]
i56 [19]	IC		2270 to 4170	k19	
i6 [19]	IC	89/11/07	2220 to 3030	i56	
lp0301	NIST VUV	02/03/01	1830 to 3194	Ge I,II [17]	Figs. 3 & 4 in [13]
fe1115	NIST VUV	02/11/15	1558 to 2689	lp0301	
fe0409.002	NIST 2-m	09/04/09	2748 to 5765	Ar II [25], Fe I,II [18, 19]	

Table 3. Comparison of wavenumbers of Fe lines in Aldenius et al. [8] and adjusted wavenumbers of Nave et al. [19]. The wavenumbers of [19] have been increased by 10.6 parts in 10^8 . The standard uncertainty in the last digits of the wavenumbers and of the levels is given in parenthesis and is dominated by the calibration uncertainty.

Species	Nave et al. (cm^{-1}) [19]	Aldenius et al. (cm^{-1}) [8]	(column 3 / column 2) - 1
Fe II	38458.9912(20)	38458.9908(20)	-1.0×10^{-8}
Fe II	38660.0535(20)	38660.0523(20)	-3.1×10^{-8}
Fe II	41968.0687(20)	41968.0654(20)	-7.7×10^{-8}
Fe II	42114.8374(20)	42114.8365(20)	-2.1×10^{-8}
Fe II	42658.2449(20)	42658.2430(20)	-4.5×10^{-8}
		Mean	$(-3.7 \pm 2.6) \times 10^{-8}$

Table 4. Comparison of adjusted wavenumbers of Mg lines in Aldenius et al. [8] with frequency comb measurements (col. 3) taken from paper listed in the reference column. The wavenumbers from [8] have been increased by 3.7 parts in 10^8 . The standard uncertainties in the last digits of the wavenumbers are given in parentheses.

Species	Aldenius (cm^{-1})	Frequency comb (cm^{-1})	(column 2/column 3) -1	Reference
	[8]			
Mg I	35051.2817(20)	35051.2808(2)	2.6×10^{-8}	[9]
Mg II	35669.3039(20)	35669.30440(6)	-1.3×10^{-8}	[11]
Mg II	35760.8523(20)	35760.85414(6)	-5.1×10^{-8}	[11]
Mg I	49346.7730(30)	49346.77252(7)	1.0×10^{-8}	[10]
		Mean	$(-0.7 \pm 3) \times 10^{-8}$	

Table 5. Determination of the z^6P levels of Fe II from transitions to the ground term around 2350 Å. The statistical uncertainty in the last decimal place of the wavenumbers is given in parenthesis. The total standard uncertainty includes the uncertainty in the calibration.

Lower level	Upper level	lower level value cm^{-1}	Wavenumber cm^{-1}	Upper level value cm^{-1}
$a^6D_{5/2}$	$z^6P_{7/2}$	667.6829(5)	41990.5610(3)	42658.2439(6)
$a^6D_{7/2}$	$z^6P_{7/2}$	384.7872(4)	42273.4573(4)	42658.2445(6)
			Mean	42658.2442(5)
			Total uncertainty	0.0011
$a^6D_{5/2}$	$z^6P_{5/2}$	667.6829(5)	42570.9226(4)	43238.6055(6)
$a^6D_{7/2}$	$z^6P_{5/2}$	384.7872(4)	42853.8188(4)	43238.6060(6)
			Mean	43238.6058(5)
			Total uncertainty	0.0011
$a^6D_{1/2}$	$z^6P_{3/2}$	977.0498(6)	42643.9332(4)	43620.9830(7)
$a^6D_{5/2}$	$z^6P_{3/2}$	667.6829(5)	42953.2994(5)	43620.9823(7)
			Mean	43620.9827(6)
			Total uncertainty	0.0012

Table 6. Determination of the $a^6S_{5/2}$ level of Fe II using transitions from the z^6P levels. The statistical uncertainties in the last digits of the wavenumber and levels are given in parentheses. The total standard uncertainty of the a^6S level includes a contribution of 4×10^{-8} times the level uncertainty due to the calibration.

Upper level	Upper level value cm^{-1}	Wavenumber cm^{-1}	a^6S level cm^{-1}
$z^6P_{7/2}$	42658.2442(5)	19340.6092(2)	23317.6350(5)
$z^6P_{5/2}$	43238.6058(5)	19920.9733(2)	23317.6325(5)
$z^6P_{3/2}$	43620.9827(6)	20303.3477(3)	23317.6350(7)
		Weighted mean	23317.6340(3)
		Total uncertainty	0.0010

Table 7. Determination of the y^6P levels of Fe II from transitions to the a^6S level. The statistical uncertainty in the last digits of the wavenumbers and levels is given in parentheses. The total standard uncertainty is common to all levels and includes a contribution of $4 \times 10^{-8} \sigma$ due to the calibration. The last column contains the level value and standard uncertainty in parenthesis with respect to the ground level obtained from the LOPT program as described in section 5 .

Upper level	Wavenumber cm^{-1}	Upper level value cm^{-1}	Level value from LOPT cm^{-1}
$y^6P_{3/2}$	38657.2997(14)	61974.9347(14)	61974.9325(24)
$y^6P_{5/2}$	38731.4041(7)	62049.0381(8)	62049.0408(27)
$y^6P_{7/2}$	38853.9885(4)	62171.6225(5)	62171.6245(27)
Total uncertainty		0.003	

Table 8. Experimental and Ritz wavenumbers for the a^6D - y^6P multiplet. The standard uncertainties in the last digits of the wavenumbers and wavelengths are given in parentheses.

Lower level	Upper level	σ_{a6S}^a cm^{-1}	σ_{exp}^b cm^{-1}	σ_{Ritz}^c cm^{-1}	λ_{Ritz}^d \AA
$a^6D_{1/2}$	$y^6P_{3/2}$	60997.884(3)	60997.882(3)	60997.8827(25)	1639.40117(7)
$a^6D_{3/2}$	$y^6P_{3/2}$	61112.322(3)	61112.321(3)	61112.3207(25)	1636.33125(7)
$a^6D_{5/2}$	$y^6P_{3/2}$	61307.251(3)	61307.247(3)	61307.2496(25)	1631.12847(7)
$a^6D_{3/2}$	$y^6P_{5/2}$	61186.426(3)	61186.432(4)	61186.4290(28)	1634.34934(7)
$a^6D_{5/2}$	$y^6P_{5/2}$	61381.355(3)	61381.358(3)	61381.3579(28)	1629.15914(7)
$a^6D_{7/2}$	$y^6P_{5/2}$	61664.251(3)	61664.255(3)	61664.2536(27)	1621.68508(7)
$a^6D_{5/2}$	$y^6P_{7/2}$	61503.940(3)	61503.945(8)	61503.9416(27)	1625.91205(7)
$a^6D_{7/2}$	$y^6P_{7/2}$	61786.835(3)	61786.837(3)	61786.8373(27)	1618.46769(7)
$a^6D_{9/2}$	$y^6P_{7/2}$	62171.623(3)	62171.626(4)	62171.6245(27)	1608.45081(7)

^aWavenumber calculated using a^6S as an intermediate level

^bExperimental wavenumber from archival spectra corrected according to section 4.B.

^cRitz wavenumber calculated from all optimized energy levels

^dWavelength calculated from the Ritz wavenumber in column 5.